Variation in n-alkane δD values from terrestrial plants at high latitude: Implications for paleoclimate reconstruction

Hong Yang a,⁎, Weiguuo Liu b,c, Qin Leng a,d, Michael T. Hren e, Mark Pagani e

a Department of Science and Technology, College of Arts and Sciences, Bryant University, Smithfield, RI 02917, USA
b State Key Laboratory of Loess and Quaternary Geology, IEE, CAS, Xi'an 710075, PR China
c School of Human Settlement and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, PR China
d LPS, Nanjing Institute of Geology and Palaeontology, CAS, Nanjing 210008, PR China
e Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA

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A B S T R A C T

The molecular hydrogen isotope composition (δD) of leaf waxes from terrestrial plants is increasingly used to infer hydrological characteristics of ancient high latitude climates. Analysis of the hydrogen isotopic composition of n-alkanes (δDn-alkane) from a global dataset of individual plants growing at low and middle latitudes indicates that plant ecological life form is an important factor in determining the hydrogen isotope fractionation. However, environmental and biological controls of high latitudinal leaf wax δD values are poorly understood because of a lack of δD records from modern flora in these regions. We previously noticed smaller apparent hydrogen isotope fractionations between n-alkanes and environmental water (δDwater) in deciduous trees growing at high latitudes (>59°N; Liu, W.-G., Yang, H., 2008). Multiple controls for the variability of hydrogen isotopic compositions in higher plant n-alkanes from modern ecosystems. Global Change Biology 14, 2166–2177.) To further examine these issues, we measured δDn-alkane from a variety of plants that inhabit high latitude environments and added critically needed leaf wax δD data from grass and herbs to the existing global δDn-alkane database. Inclusion of these new data with the existing global dataset (n = 408) confirms plant ecological life form as an important control for leaf wax δD variation for terrestrial plants living at high latitudes. Our results suggest that, while precipitation δD is captured in these high latitude plants, physiological characteristics such as leaf area, venation pattern and hydraulic system, that enhance transpiration rate during summer growth, may impart δDn-alkane differences among plants with different ecological life forms.

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1. Introduction

The hydrogen isotopic composition of plant leaf waxes preserved in sediments is becoming an increasingly important tool in the reconstruction of ancient hydrologic conditions. However, records of the hydrogen isotopic composition of plant n-alkanes (δDn-alkane) from high latitudes are limited and our understanding of the factors affecting the apparent hydrogen isotope fractionation between n-alkanes and environmental water (δDwater) is still developing. An improved understanding of ƒalk-water ultimately comes from the study of the δDn-alkane variation in identifiable individual plants because the biology and ecology of the plants are known, and physiological experiments can be designed in greenhouses or growth chambers to test the cause and consequence of observed δD variation.

Early studies of δDn-alkane values of living plants focused on documentation of δD variation from various types of plants, the distribution of δD values for lipids with different chain length and their relationship with δ13C values for the same compounds (Sessions et al., 1999; Chikaraishi and Naraoka, 2003; Yang and Huang, 2003; Bi et al., 2005). Subsequent studies explored the effects of n-alkane synthesis (Chikaraishi et al., 2004, 2005), seasonality (Sessions, 2006; Sachse et al., 2009), plant ecological life forms (Liu et al., 2006), same site variation (Hou et al., 2007), rooting patterns (Krull et al., 2006) and climate gradient (Sachse et al., 2006; Duan and Wu, 2009). Using the available global n-alkane δD record, Liu and Yang (2008) identified and ranked multiple controlling factors and their impact on the variation of δD values of higher plant waxes. They also observed a smaller ƒalk-water from deciduous trees living at high latitude and anticipated δD depleted hydrogen isotope values for grass leaf waxes from the same regions. A recent greenhouse experiment using deciduous conifers grown under a simulated Arctic environment further illustrated high latitude effects on hydrogen isotope fractionation caused by enhanced leaf transpiration under 24 h continuous light illumination (Yang et al., 2009).
Here, we present $\delta D_{n}$-alkane records of grasses and other plants from high latitude regions (>59°N). These new data, in combination with published records, are used to examine $\delta D_{n}$-alkane differences between plants living at high and mid/low latitudes, with a focus on the influence that ecological life form has on determining $\delta D_{n}$-alkane values. Our results have significant implications for the application of n-alkane $\delta D$ data as a paleoclimate proxy and in particular, to high latitude paleohydrology.

2. Materials and methods

We analyzed the $\delta D_{n}$-alkane values of 26 leaf samples collected from a range of high latitude environments (>59°N; Table 1). Among these, 15 were collected from Northern Europe (Sweden and Finland) and the rest were from North America (Alaska and Canadian Arctic). Except for one C4 plant (Zea mays L.) from Sweden and one horsetail (Equisetum pretense Ehrl) from Alaska, the samples derive from 16 grass/herb species and 8 tree/shrub species that utilize the C3 photosynthetic pathway (Table 1). Because of the low occurrence and the difficulty in collecting fresh grass species at high latitude, we supplemented our samples with six herbarium grass specimens collected from Finland in 1983.

Leaves were cleaned with distilled water to remove dust particles, dried at 40 °C and extracted with dichloromethane (DCM). Hydrogen isotope analysis was performed using a HP 6890 gas chromatograph, interfaced via a high temperature conversion interface to a Thermo Finnigan MAT 253 mass spectrometer (Hilkert et al., 1999). The gas chromatography (GC) temperature program was: 80 °C (1 min) to 180 °C at 3 °C/min and then to 300 °C (held 10 min). Separated components were directed to H$_2$ by way of a pyrolysis reactor at 1445 °C. The $\delta D$ values were calibrated against H$_2$ reference gas calibrated via a co-injected laboratory working standard (n-C$_{16}$ and n-C$_{30}$ alkanes, and 5α-androstan; isotopic ratio values determined offline by A. Schimmelmann, Biogeochemical Laboratory at Indiana University).

Each sample was analyzed three times; H$_2$ factors were calculated daily using the same H$_2$ reference gas. The precision of isotopic measurements of H$_2$ reference gas after H$_2$ factor correction was 1‰ or better. Analytical error was <4‰ for samples; $\delta D$ values are expressed relative to the VSMOW standard using Eq. (1).

$$\delta D = 1000 \times \left( \frac{\text{H}^2\text{O}_{\text{sample}}}{\text{H}^2\text{O}_{\text{VSMOW}}} - 1 \right)$$

Leaf wax D/H ratio values from C$_{27}$, C$_{29}$ and C$_{31}$ n-alkanes are highly correlated (Liu and Yang, 2008), so we used an amount-weighted mean $\delta D$ value of the three compounds for our interpretations, as practised in other recent studies (e.g. Smith and Freeman, 2006; Feakins and Sessions, 2010). Pearson correlation was conducted to investigate various correlations between $\delta D$ values of n-alkanes and various geographic and environmental factors. One-way ANOVA tests were used to examine the statistical significance of different relationships; $\varepsilon_{\text{alk-water}}$ was calculated from the following relationship:

$$\varepsilon_{\text{alk-water}} = 1000 \times \left[ \left( \delta D_{\text{n-alkane}} + 1000 \right) / \left( \delta D_{\text{water}} + 1000 \right) - 1 \right]$$

3. Results and discussion

3.1. Distribution of leaf wax $\delta D$ in high latitude plants

Our new data (Table 1) indicate that $\delta D_{n}$-alkane values from high latitude plants fall into two distinct groups based upon plant ecological life form, including woody trees/shrubs and grasses/herbs. Grasses and herbs tend to possess relatively lower $\delta D$ values relative to trees/shrubs at given latitudes (Fig. 1). The $\delta D_{n}$-alkane values from grasses and herbs range from ~171‰ to ~307‰, with the lowest value for Alopecurus alpinus J.E. Smith, a C$_3$ grass from Axel Heiberg Island in Canada at 80°N. In contrast, the values for woody plants span a range from ~151‰ in Castanea sativa Mill (60°N) to ~262‰ from Salix arctica Pall. (woody deciduous shrub from Axel Heiberg Island). Except for one C$_4$ species (Zea mays L.) with a $\delta D$ value of ~228‰ (59°N), all the species are C$_3$ plants. Significant $\delta D$ variation (up to 89‰) is evident from the range of plants evaluated at the same site.

These data, in combination with published records from high latitude deciduous plants (Sachse et al., 2006), indicate that $\delta D_{n}$-alkane values track the hydrogen isotope compositions of precipitation as the first order control, which is further modified by plant ecological life form (Fig. 1). While $\delta D_{n}$-alkane signals from plants of both life forms record precipitation $\delta D$, these correlations have different slopes and can be clearly separated into two groups: grass vs. woody plants. The pattern and range of $\delta D_{n}$-alkane differences between grass and trees are consistent with our previous observations from middle and low latitudes (Liu et al., 2006; Liu and Yang, 2008). Regression analysis revealed three general patterns: (i) Correlation R$^2$ values were similar whether modeled annual or summer precipitation $\delta D$ values were applied; (ii) correlation can be significantly improved if different plant ecological life forms (trees/shrubs vs. grasses/herbs) were considered. (iii) A better correlation was obtained between $\delta D_{n}$-alkane values from grasses/herbs and precipitation than trees/shrubs or integrated trees mixed with grasses.

3.2. Global $\delta D_{n}$-alkane distribution

Fig. 2 displays the correlations between available n-alkane $\delta D$ values from identifiable living plants (n = 408) and modeled mean annual precipitation $\delta D$ values at these sites (Bowen and Revenaugh, 2003). The general pattern is similar to that of an analysis using middle and lower latitude data (Fig. 4b in Liu and Yang, 2008) with grass and woody plants clearly separated. Slopes for both woody trees/shrubs and grasses/herbs have slightly changed, especially for $\delta D$ values in grasses/herbs which display a lower slope with the addition of new high latitude data. Differences in slopes between the two ecological life forms are distinct and statistically significant (p < 0.01). Although both Correlation R$^2$ values (Fig. 1) are lower (0.31 for grasses and 0.28 for woody plants) compared with the high latitude data alone (0.85 for grasses and 0.53 for woody plants) because of the large variation in $\delta D_{n}$-alkane in the global database, the distinguishable distribution patterns between leaf $\delta D_{n}$-alkane values from grass and woody plants with respect to global precipitation $\delta D$ remain apparent.

3.3. High latitude effect on hydrogen isotope fractionation

A high latitude effect on $\varepsilon_{\text{alk-water}}$ is apparent in Fig. 3. The $\delta D_{n}$-alkane values and $\varepsilon_{\text{alk-water}}$ relationships for both woody deciduous trees and grasses/herbs from middle and low latitudes exhibit a similar linear relationship and $\delta D_{n}$-alkane values from woody plants show slightly lower $\varepsilon_{\text{alk-water}}$ values than those from grasses, as indicated by the trend lines. Correlation R$^2$ values indicate a tighter correlation between $\varepsilon_{\text{alk-water}}$ and middle and lower latitude $\delta D_{n}$-alkane from grasses (0.94) than that from woody plants (0.88). However, $\delta D_{n}$-alkane signals from high latitude plants deviate from this middle and low latitude linear relationship, the deviation being driven by low $\varepsilon_{\text{alk-water}}$ values. This occurs for woody deciduous trees as well as grasses and herbs at the high latitudes, with woody plants having slightly smaller $\varepsilon_{\text{alk-water}}$ values. We attribute the expression of lower high latitude $\varepsilon_{\text{alk-water}}$ values to higher transpiration rates and other physiological effects caused by increasingly longer daily intervals of photosynthesis associated with increasing latitude.
<table>
<thead>
<tr>
<th>Taxon</th>
<th>Family</th>
<th>Life Form</th>
<th>Location</th>
<th>Coordination</th>
<th>$C_{27}$</th>
<th>$C_{29}$</th>
<th>$C_{31}$</th>
<th>Mean</th>
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<td>-182 0.1</td>
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<td>n.d.</td>
<td>n.d.</td>
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<td>145 1.4</td>
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<td>-161 1.2</td>
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<td>n.d.</td>
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<td>-251 0.4</td>
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<td>-248 0.6</td>
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*a $\delta D$ values are expressed in $\%$ relative to VSMOW.

*b SD = standard derivation of three measurements.
mental and biological factors (Sachse et al., 2006; Liu and Yang, 2008). Our new data and published information demonstrate that the ΔD of precipitation and plant physiology exerts primary influences on εalk-water. Previous studies have shown that evaporation of soil water (Hou et al., 2008), temperature (Duan and Wu, 2009), rooting pattern (Krull et al., 2006), plant systematics (angiosperms vs. gymnosperms; Pedentchouk et al., 2008), water use efficiency (Hou et al., 2007b) and rate of leaf transpiration (Yang et al., 2009; Feakins and Sessions, 2010) also influence the distribution of ΔDn-alkane. Variation at a given site. While the amount of lipid ΔD variation among plants growing at the same high latitude site is consistent with previous reports (Chikarashki and Naraoka, 2003; Liu et al., 2006; Hou et al., 2007a; Feakins and Sessions, 2010), our new n-alkane ΔD data provide additional support for the link between ΔD variation and plant ecological life form (Liu et al., 2006). As Fig. 1 illustrates, the distribution of ΔD values from grasses and herbs can be separated from that of shrubs and trees, with a lack of evidence for ΔD variation as a result of plant systematics (i.e. angiosperms vs. gymnosperms) or photosynthetic pathways.

We posit that higher ΔDn-alkane values of woody plants reflect higher rates of leaf water transpiration during high latitude summer months than for grasses, preliminarily because of their characteristics by way of leaf area and denser and more orderly venation patterns that increase hydraulic conductance (Brodbibb et al., 2007; McKown et al., 2010). Hydrogen isotopic enrichment in leaf water during transpiration is well known (Leaney et al., 1985, see also Farquhar et al., 2007 and Barbour, 2007 for recent reviews), but there is a lack of understanding for how the D-enriched leaf water influences ΔDn-alkane signatures. In a greenhouse experiment Yang et al. (2009) detected that, under 24 h simulated arctic environment, some deciduous conifers can lose up to 2.4 times more water per day than that under regular diurnal light at lower latitudes, and this transpiration effect resulted in D enrichment of leaf water attributed to have produced up to 40% heavier ΔDn-alkane in grasses (McInerney et al., 2011, but see Brader et al., 2010 for

**4. Implications**

The apparent hydrogen isotope fractionation between plant leaf wax and environmental water is controlled by multiple environmental and biological factors (Sachse et al., 2006; Liu and Yang, 2008). The negative correlation between mean Northern Hemisphere precipitation and the D enrichment in leaf water of woody plants (Fig. 1) and grasses (Fig. 2) suggests that these environmental factors control the D-enrichment in leaf water. The D enrichment in leaf water is likely to be controlled by the D enrichment in precipitation, which is consistent with previous studies (Bowen and Revenaugh, 2003).
minimal evaporation effect on *Sphagnum*. In the above cases, leaf water was not measured, leaving room for a direct assessment of the impact of D-enriched leaf water on $\delta_{D_{\text{alkane}}}$ due to transpiration. It is possible that, as a result of different physiological characteristics, such as leaf area, venation pattern, hydraulic system and different timing for lipid synthesis between woody plants and grasses (Koch et al., 2004; Richardson et al., 2005), the impact of transpiration on $\delta_{D_{\text{alkane}}}$ signals is different between these two major plant groups with different ecological life forms. If this is true, then it may help explain the profound and consistent pattern of heavier $\delta_{D_{\text{alkane}}}$ in woody plants relative to that in grasses at a given site (Fig. 2).

Our results have several implications for high latitude paleoclimate interpretations based on $\delta_{D_{\text{alkane}}}$ values. First, as apparent $v_{\text{alk-water}}$ for plants living at high latitude is 20–50% smaller than at lower latitudes, $\delta_D$ in ancient precipitation can be overestimated if a globally averaged $v_{\text{alk-water}}$ value is applied. Second, as grasses and woody trees fall into distinct isotopic fields, it is important to understand the specifics of the ecosystem in order to distinguish whether $\delta_D$ change was due to a change of vegetation or climate. Thus, paleovegetation information obtained from traditional paleobotanic and palynological methods should be consulted when interpreting $\delta_D$ data from sediments. Third, as both $\delta_{D_{\text{alkane}}}$ and $v_{\text{alk-water}}$ vary across different plant taxa, specific fractionation factors calibrated for an individual taxon may be used in collaboration with the reconstruction of paleo-precipitation $\delta_D$ based upon lipids from sediments, especially in high latitude regions. It has been noticed (Sachse et al., 2004; Hou et al., 2008; Polissar and Freeman, 2010) that $\delta_{D_{\text{alkane}}}$ values for lipids extracted from sediments and soils usually have a closer correlation with $\delta_D$ in precipitation, presumably because of an ecosystem-wide averaging effect of lipid isotope signals. While the range and mechanism for the isotopic averaging effect are not well understood, an ecosystem-wide difference in $v_{\text{alk-water}}$ complicates the reconstruction of $\delta_D$ in regional precipitation (Polissar and Freeman, 2010; Mclnerney et al., 2011). Taxon-specific $\delta_D$ studies based upon taxon-specific fractionation factors calculated from controlled experiments (Yang et al., 2009; Nichols et al., 2009; Brader et al., 2010; Mclnerney et al., 2011) should shed more light on the mechanism of the process. Finally, the application of $\delta_D$ values generated from herbarium specimens for studies of recent climate changes has not been explored and our study demonstrates the feasibility of utilizing herbarium specimens, collected from historical times or regions that are now difficult to access, as a viable resource for compound-specific hydrogen isotope analysis.

5. Conclusions

Leaf $\delta_{D_{\text{alkane}}}$ data obtained from plants living at high latitude ($>$59°N) provide further evidence for multiple controls on D/H composition of plant leaf waxes and $v_{\text{alk-water}}$, extending the general trend predicted by Liu and Yang (2008) to higher latitudes. Our results further demonstrate that plant ecological life forms play an important role in controlling $\delta_{D_{\text{alkane}}}$ values. Physiological characteristics that impact on leaf transpiration rates are likely responsible for some of the observed $\delta_D$ variation in woody plants, as well as for the appearance of smaller $v_{\text{alk-water}}$ values for high latitude plants. Our results point toward the importance of understanding ecosystem changes when interpreting n-alkane $\delta_D$ data from sediments.

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